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Structure engineering of WO_3 nanoparticles for porous film applications by advanced reactive gas deposition

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Abstract

Fine-grained crystalline or amorphous thin films are normally produced by atomistic deposition of species under conditions giving a low adaton mobility. Here we consider an alternative high-temperature route employing advanced reactive gas deposition for structure engineering of WO_3 nanoparticles in making nanocrystalline films, especially, for gas sensing applications. For instance, structure engineering may be necessary in the case of very fine-grained n-type semiconductor oxide films in order to increase the electrical conductivity of the films. The crystal structure of WO_3 together with its different phases makes possible structure engineering of its nanoparticles by high-temperature processes such as the reactive gas deposition. Produced nanocrystalline WO_3 films in metastable tetragonal crystal structure were found to be very sensitive to H_2S in air already at room temperature.

Keywords: Electrical properties; Films; Microstructure; Sensors; WO_3

1. Introduction

There has been an increasing interest during the last years in the study of nanocrystalline materials owing to their many novel and improved properties in comparison with those of conventional coarse-grained structures.[1,2] The surface-to-bulk ratio for a nanocrystalline material is much greater than for a material with large grains, and in the case of ceramics these materials may have a large porosity. The porosity yields a large interface between the solid and a gaseous medium.

The conductance of semiconductor gas sensors changes when the composition of the surrounding atmosphere is altered.[3] It is well known that the gas sensitivity of porous SnO_2 [4] and WO_3 [5] films increases with decreasing grain size. The interaction between a gas and a solid mainly takes place on the surface and, therefore, the amount of atoms residing in grain boundaries and at interfaces is critical for controling the properties of the gas sensor. It is not uncommon that the portion of the surface atoms exceeds 50% in a nanocrystalline material.[1,2] There are only a few studies of the gas sensing properties of nanocrystalline WO_3 films. Direct evaporation of tungsten in the presence of O_2 [6] and "soft chemistry" [7] have been used for the fabrication of the films. In this work, we take an alternative route and employ advanced reactive gas deposition [8,9] to make nanocrystalline films of WO_3. The gas deposition method comprises evaporation of metallic tungsten in the presence of synthetic air so that well defined crystalline precursors for film manufacturing are formed.

The H_2S sensitivity of the WO_3 films annealed at different temperatures was studied both in dry synthetic air and in argon together with structure characterization of the films.

2. Reactive gas deposition of films

Nanocrystalline WO_3 films were produced by an advanced gas deposition unit (Ultra Fine Particle Equipment, ULVAC Ltd., Japan). A schematic of the equipment is shown in Fig. 1. An evaporation and condensation chamber, and a deposition chamber, were evacuated to 3×10^{-2} mbar, and about 13 mbar (10 l/min) of dry synthetic air (80% N_2 and 20% O_2) was introduced into the former of these chambers. A highly

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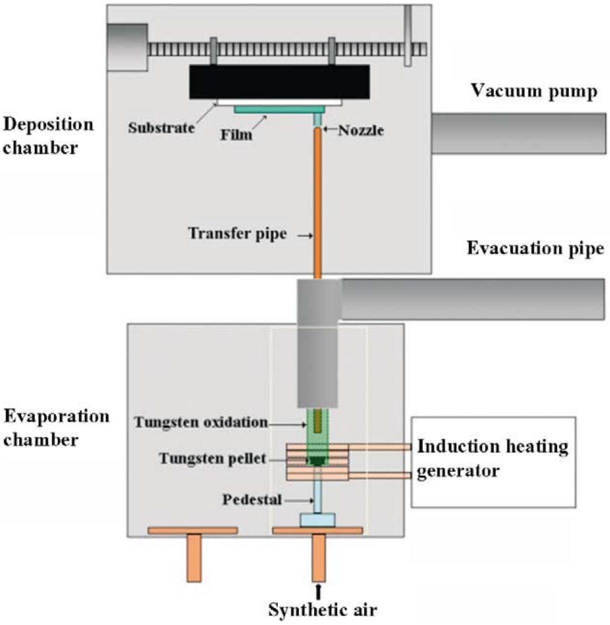

Fig. 1. Schematic picture of the advanced reactive gas deposition equipment.

laminar gas flow was then created, which led to particle growth under near-equilibrium conditions with only a weak tendency towards agglomeration. The particles have a narrow size distribution.[10] The starting material, which was a tungsten pellet (99.95% purity), was installed in the evaporation and condensation chamber, where the heating ($\sim$1450 K) and oxidation of the tungsten occurs. The heating is provided by an induction coil of copper. The formed particles are carried through a transfer pipe with the gas flow and are ejected out of a nozzle into an evacuated deposition chamber for films formation on a substrate. The substrates were mounted on a table that can be scanned along the x, y and z directions by a digital programmable controller. The scanning speed of the substrate was 1.5 mms^{-1}. Alumina substrates were used with preprinted gold electrodes and with a Pt heating resistor printed on the reverse side. Rectangular films (3×2.5 mm^2) of nanocrystalline WO_3 were deposited onto the gold electrodes. The thickness of the films was measured using a Tencor Alpha-Step 200 mechanical stylus instrument with a vertical resolution of 0.5 nm. The average thickness of the film was 11 μm. The sintering of the films was carried out by heating in air at temperatures τ_s in the $100<\tau_s<600$ °C range.

3. Structural characterization

The crystal structure and mean crystallite size of the nanocrystalline WO_3 films were obtained from X-ray diffraction measurements using a Siemens D5000 diffractometer operating with CuK_α radiation and equipped with a Göbel mirror and a parallel plate collimator. The microstructure of the films was analyzed by scanning electron microscopy (SEM) using a LEO 1550 instrument with a Gemini column and by high resolution transmission electron microscopy (HRTEM) using a Jeol 2000 FX II (200 kV) and a Tecnai F 30 (300 kV) instrument with a point resolution of 0.14 nm.

Fig. 2 shows X-ray diffraction patterns obtained from WO_3 films directly after deposition and after sintering at 100, 200, 300, 400, 500 and 600 °C. Reflection peaks of both monoclinic (m) and tetragonal (t) phases of WO_3 and of the substrate (Al_2O_3) are seen in the figure. The grain size was estimated from Scherrer's formula [11]. The as-deposited nanocrystalline WO_3 films are built up from metastable tetragonal phase crystallites (twin peaks from (001) and (110) reflections) that are $\sim$10 nm in diameter. The tetragonal structure corresponds to the high temperature phase of WO_3 stable above 1010 K, and at room temperature the stable phase is monoclinic. Clearly, the high temperature associated with the W oxide evaporation during film fabrication can produce the tetragonal phase, which stays metastable during cooling in the gas stream. In WO_3 films sintered up to 300 °C, the crystal structure was tetragonal and no grain growth was found. For $\tau_s>400$ °C, there is a phase transition with a monoclinic phase appearing in the film together with grain growth. At $\tau_s=600$ °C, the monoclinic structure is dominating, and the grain size is $\sim$35 nm.

SEM studies of as-deposited films showed a smooth surface without cracks. The SEM micrograph in Fig. 3 illustrates the morphology of the films after sintering at $\tau_s=300$ °C. The sintering of the films produced some cracks on the film surface, possibly as a result of a stress relief during grain growth and phase transition. The

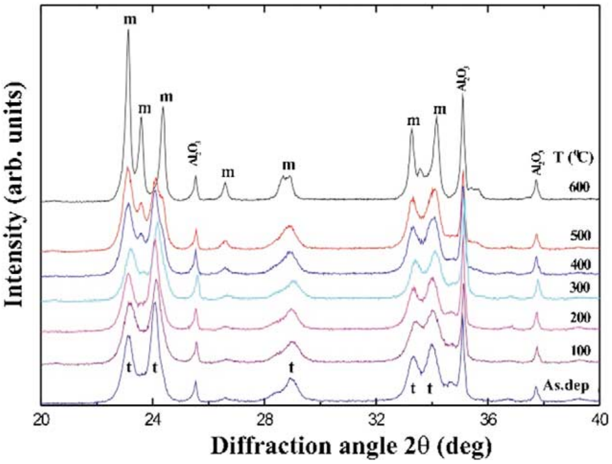

Fig. 2. X-ray diffraction patterns measured with CuK_α radiation from as-deposited and sintered ($100 < \tau_s < 600$ °C) nanocrystalline WO_3 films.

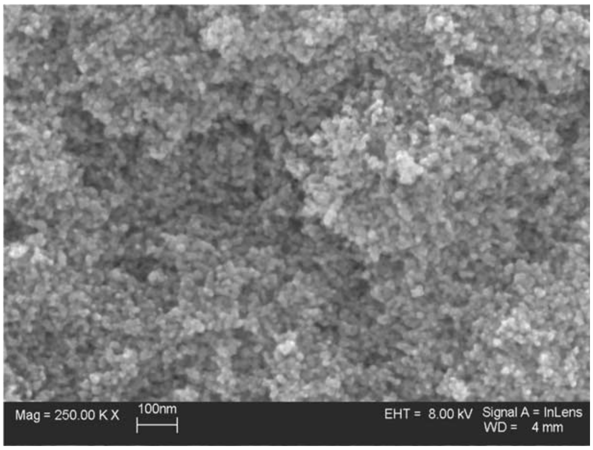

Fig. 3. SEM micrograph from a nanocrystalline WO_3 film sintered at 300 °C.

micrograph of the nanocrystalline WO_3 film in Fig. 3 shows a very porous structure. The pores have linear extents of ~10 nm, and hence their dimensions are similar to the dimensions of the grains.

HRTEM images were used to study possible defects on as-deposited nanocrystalline WO_3 film surfaces. A lot of defects were found on some surfaces.

4. Gas sensing properties

The electrical conductance of the WO_3 films was obtained by measuring the current through the film at a constant voltage of 1 V. The samples under test were placed in a stainless steel chamber (500 cm^3) and exposed to different gas concentrations. Gas-sensing properties of the films were studied at various operating temperatures τ_o in the $300 < \tau_o < 800$ K range with a computer-controlled measuring system employing the flow-through principle.

The conductance response at gas exposure is defined as the conductance ratio G_{gas}/G_{air}, where G_{gas} and G_{air} denote the conductance in the test gas and in dry synthetic air, respectively. G_{gas} was measured as a function of time after the gas was introduced into the chamber. The sintering temperature was found to have an important role for the gas sensing properties of the films. Fig. 4 shows the conductance response at six temperatures τ_o between 300 and 800 K of a nanocrystalline WO_3 film sintered at 300 °C at exposure to 10 ppm of H_2S in dry synthetic air. The highest conductance response took plase at the operation temperature $\tau_o = 400$ K. The conductance of the film increased by about a factor of 3500 after 17 min of exposure to 10 ppm of H_2S at 400 K. At room temperature, the increase was by a factor of about 700 in Fig. 4(a). The sensitivity of the film was found to decrease for increasing operation temperatures above 400 K, as shown in Fig. 4(b). The conductance recovery after H_2S exposure was slow at low operation temperatures and, especially, at room temperature it may take many hours to be complete. However, a short heating pulse (about 1 min) up to 250 °C after the exposure to H_2S at room temperature brought the conductance rapidly to its initial value.

The similar set of experiments shown in Fig. 4 were made with the same sensing WO_3 film also at exposure to 10 ppm of H_2S in dry argon. In that case, the conductance response was very low. At low operation temperatures below 500 K, the values of the conductance response were less than 1% of the values at H_2S exposure in synthetic air in Fig. 4.

The conductance responses of the nanocrystalline WO_3 films at exposure to oxygen in dry nitrogen were also measured at different operation temperatures. A conductance decrease by a factor of about 200 was usually found when dry nitrogen was changed to dry synthetic air (20% of O_2 in N_2).

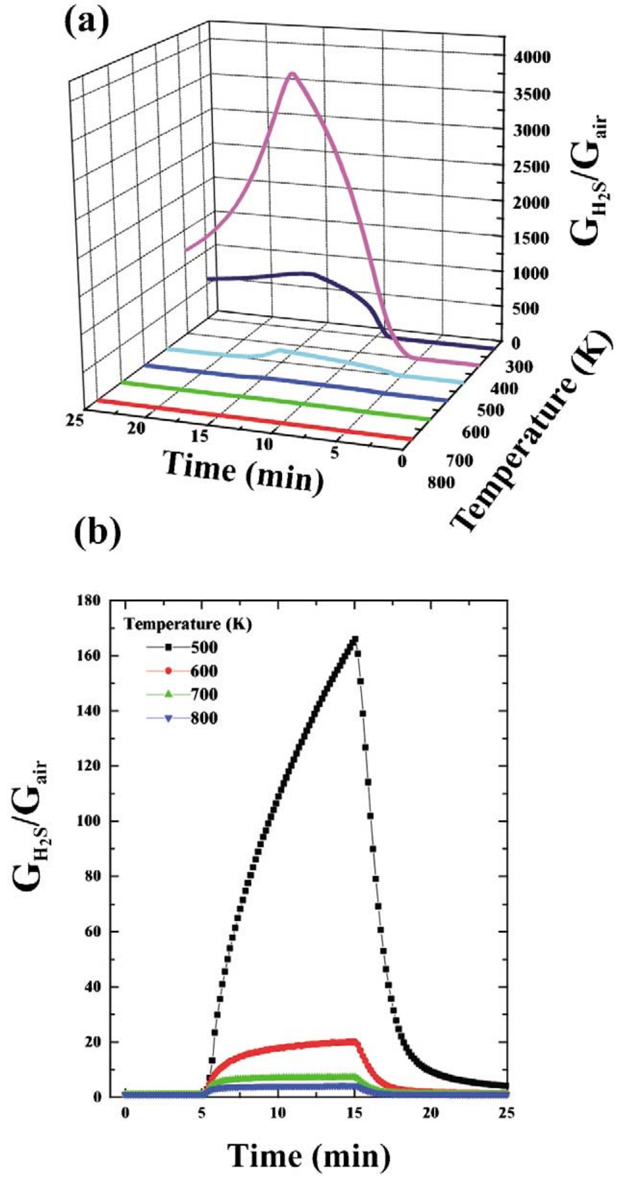

Fig. 4. Conductance response as a function of time of a nanocrystalline WO_3 film sintered at 300 °C at exposure to 10 ppm of H_2S in dry synthetic air at temperatures of (a) 300, 400, 500, 600, 700 and 800 K and (b) in addition in lower scale at 500, 600, 700 and 800 K.

5. Discussion

Oxygen in the ambient atmosphere of the nanocrystalline WO_3 films seems to be a critical constituent for the high H_2S sensitivity of the films at low operation temperatures like the room temperature. In the case of cubic ReO_3 structure for WO_3 (in fact, WO_3 phases are derived from the ReO_3 structure) there are W^{6+} ions at the cube corners surrounded by oxygen octahedra. The structure resembles the ABO_3 perovskite structure where A-site cations occupy the big empty cuboctahedral cages at the cube centres in the ReO_3 structure. Terminal oxygen at the grain surfaces may be critical for the high H_2S sensitivity of the films. Electrochemical and optical measurements indicated strong electrochromism upon Li^+ insertion/extraction in the films and infrared absorption spectroscopy discovered strong LO vibration modes at ~950 cm^{-1}, mainly stemming from $W=0$ terminal bonds on internal surfaces of the film.[12] It was also found that the LO modes due to the terminal $W=0$ bonds disappear upon Li^+ intercalation,[12] which means that terminal oxygen leaves the surface releasing electrons into the grains and increasing the film conductivity. Similar effects have been found to relate to vibrational spectra of W oxide films upon both Li^+ and H^+ insertion. H^+ insertion to the nanocrystalline WO_3 films from the dissociation of H_2S at grain surfaces may be the reason for the high H_2S sensitivity of the films in our experiments. It gives also an explanation for the critical role of oxygen in the ambient atmosphere for the high sensitivity.

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